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SURVEY OF INDUSTRIAL PROCESSING DATA

TASK II - POLLUTION POTENTIAL OF POLYBROMINATED BIPHENYLS

MIDWEST RESEARCH INSTITUTE

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

JUNE 1975

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ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
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Task II - Pollution Potential of Polybrominated Biphenyls

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JUNE 1975

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PREFACE

This report presents the results of Task II of a project entitled "Survey of Industrial Processing Data." This study, "Pollution Potential of Polybrominated Biphenyls," was performed by Midwest Research Institute (MRI) under Contract No. 68-01-2105 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. The MRI Project No. was 3822-C.

This study was conducted from 1 December 1974 to 6 June 1975 under the supervision of Dr. E. W. Lawless, Head, Technology Assessment Section. Mr. C. E. Mumma, Senior Chemical Engineer, served as project leader. Other MRI personnel who contributed significantly to this study include Mr. D. Wallace, Junior Analyst, and Mr. D. Punzak, Junior Chemical Engineer.

The final report for this study was prepared by Mr. Mumma and Mr. Wallace with assistance from Dr. Lawless.

Approved for:

MIDWEST RESEARCH INSTITUTE

for H. M. Hubbard, Director
Physical Sciences Division

10 July 1975

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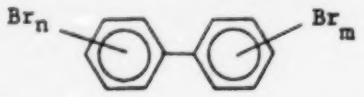
I. INTRODUCTION

Polybrominated biphenyls (PBB's) are a class of chemicals first produced in the U.S. in commercial quantities in 1970, about 40 years after introduction of their chlorinated analogues, the PCB's. The PBB's have been produced domestically on a limited scale for use as flame-retardant additives in commercial plastic products. Some of these products have toxic properties and are, therefore, sold only for applications in which the end-use product is not exposed to any food materials or contained in any fabrics subject to human exposure.

The PBB's which have been produced domestically include Firemaster BP-6, octabromobiphenyl and decabromobiphenyl. The structure and chemical composition of these products are as follows:

Firemaster BP-6

General structure

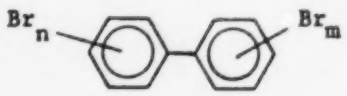


$n + m = 6$

Composition: BP-6 is a mixture of brominated biphenyls (i.e., tetra-, penta-, hexa-, hepta-, and others) with an average hexabromobiphenyl content of about 63%. Several structural isomers of each of these brominated biphenyls are possible and probably present in BP-6.

Octabromobiphenyl

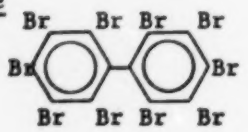
General structure



$n + m = 8$

Decabromobiphenyl

General structure



Bromine content, 82% minimum

During the spring of 1973 a quantity of a polybrominated biphenyl, produced for use as a fire-retardant chemical, was mistaken for a feed-supplement (magnesium oxide), and inadvertently added to dairy cattle feed in Michigan. Cross-contamination of other animal feeds subsequently occurred in feed mills and this accidental contamination caused much public concern about PBB's. By June 1974, the accidental contamination of cattle had spread to 20 dairy herds in Michigan, and the FDA was testing cheese, butter and condensed milk for brominated biphenyl residues.[1/] In 1974, dairy cows and milk were sampled in Michigan and eight other states for violative PBB residues by the USDA and the FDA.[2/] In February 1975, it was reported that large numbers of Michigan farm animals and food products contaminated with PBB had been destroyed and buried.[3/] As a result of this incident, Farm Bureau Services, Michigan Chemical Corporation, and their insurers spent or committed $11.5 million to pay damage claims,[3/] and litigation was underway in February 1975 to the extent of about $275 million.

Because of this recent incident of PBB contamination and concern about the potential environmental and health hazards of these substances, the Office of Toxic Substances, EPA, directed MRI to undertake this study on 1 December 1974. Much of the effort was designed to identify possible sources and effects of brominated biphenyl compounds in the environment.

The scope of work for this task included the following major activities:

1. Identification of production sites and estimation of production volumes.

2. Characterization of manufacturing processes, by-products, contamination, and risks.

3. Characterization of waste disposal practices used in manufacturing operations.

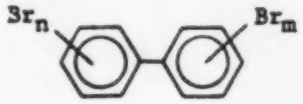
4. Descriptions of uses and substitutes for brominated biphenyl products.

5. Descriptions of environmental and health aspects.

The following sections of this report discuss methodology and the results obtained in each major activity.

II. SUMMARY

A class of chemicals, known as polybrominated biphenyls (PBB's), has been produced domestically on a limited scale for use as flame-retardant additives in plastic products. Until recently, the commercial PBB's were Firemaster BP-6 (a mixture of brominated biphenyls with various structural isomers of hexabromobiphenyl as the principal constituents), octabromobiphenyl and decabromobiphenyl. The bromine content of these products ranges from about 63% for BP-6 to about 82% for decabromobiphenyl. The structure of BP-6, the principal PBB product in the U.S., is as follows:



$n + m = 6$

In addition to the three commercial PBB products, laboratory (kilogram) quantities of monobromobiphenyl and dibromobiphenyl are also sold by domestic suppliers.

Firemaster BP-6 was involved in an animal-feed contamination incident in Michigan in 1973, when it was mistaken for a feed-supplement (magnesium oxide) and inadvertently added to dairy cattle feed. This incident caused an agricultural calamity in the state, and stimulated research studies of the potential environmental and health hazards of PBB's.

The present study, conducted during the period of 1 December 1974 to 6 June 1975, was made to help the EPA evaluate the potential for environmental contamination by brominated biphenyls.

The information collection and evaluation activities were designed to identify sources of brominated biphenyls and the environmental and health effects of these substances.

The scope of the study included identification and evaluation of production sites and volumes, manufacturing processes and waste disposal practices, commercial uses and substitutes for products and environmental and health aspects.

Sources of information for the project team included several standard reference publications, technical literature for the chemical process industry and telephone and letter inquiries to producers, consumers, and government agencies.

The major findings in this study are briefly described in the following subsections.

1. Chemical production volumes, sites, and manufacturers: During the last decade, only two domestic chemical companies produced brominated biphenyl compounds on a commercial basis. Commercial production started in 1970 and was discontinued in 1974, apparently because of one contamination incident and the risk of other environmental or health hazards. These companies, their production sites, and the compounds of interest they formerly produced, are:

* Michigan Chemical Corporation (a subsidiary of Northwest Industries) at St. Louis, Michigan, produced Firemaster BP-6, a mixture of polybrominated biphenyls consisting principally of hexabromobiphenyl. A company spokesman has reported that this plant was shut down in November 1974, and that inventory stocks of BP-6 were still being sold in April 1975.[4]

* White Chemical Corporation at Bayonne, New Jersey, produced octabromobiphenyl and decabromobiphenyl. According to a company spokesman, this production was discontinued in 1973.[5]

Michigan Chemical produced a total of about 5,088,435 kg of Firemaster BP-6, during the period of 1970 to 1975,[4] and White Chemical Corporation produced about 45,350 kg of octabromobiphenyl plus decabromobiphenyl from 1970 to 1973.[5]

There are about nine domestic chemical suppliers of brominated biphenyls who have either custom-produced or imported small quantities of these chemicals sometime during the last 10 years. The annual sales volume for any one supplier is reported to be a maximum of about 2 kg/year. The principal products are monobromobiphenyl and dibromobiphenyl.

No evidence was found that significant quantities of brominated biphenyls are imported into the U.S.; imports apparently amount to kilogram quantities at most.

2. Manufacturing processes that produce brominated biphenyls: Information on production methods was not available from domestic producers because the companies consider such operations to be proprietary. A survey of patent literature provided some detailed data on manufacturing processes. The U.S. patents of interest to this study describe preparation methods which involve reaction of biphenyl with bromine (Br_2) or bromine chloride (BrCl) in the presence of a catalyst. The major by-products are hydrogen bromide and/or hydrogen chloride.

PBB's may also be unintentionally produced in the manufacture of other brominated carbon compounds, as discussed in the next subsection of this summary, but definitive data are unavailable.

3. Waste disposal in manufacturing PBB's: In May 1975, the Permit Branch of EPA provided MRI with copies of all permit application data for waste disposal by the Michigan Chemical Corporation at their St. Louis, Michigan, plant.[6] MRI has evaluated these data, as well as information reported for a water pollution study of the same facility conducted by the Michigan Bureau of Water Management. Results of this evaluation show that measurable quantities of PBB's (0.1 to 104 μg/liter) are contained in the waste outfalls from manufacturing facilities which are not associated with the direct production of PBB's and from one facility associated with PBB manufacture. A preliminary assessment by MRI indicates that some probable sources of PBB generation in these manufacturing operations are:

* The recovery and reuse of bromine from by-product hydrogen bromide (HBr) that is contaminated with PBB's.

* The coupling of molecules of polybromobenzenes in the production of hexabromobenzene.

* The bromination of biphenyl present as an impurity in biphenol A feed materials.

* Losses to waste of some PBB's directly produced in the manufacture of Firemaster BP-6.

Results of the water pollution study showed that measurable concentrations of PBB's were present in river water samples and in fish samples taken 12.9 km downstream from the plant (i.e., 0.01 to 3.2 μg/liter for river water and 0.09 to 1.33 ppm in fish).

4. Commercial uses and substitutes for PBB's: Recent uses for Firemaster BP-6, the principal PBB compound produced domestically, are shown in the tabulation on the following page.

MRI identified two major domestic consumers of BP-6: Borg-Warner Corporation and Standard T Chemical Company. For all applications, BP-6 is thoroughly blended into various plastic resins at temperatures above the melting point of the PBB mixture. These impregnated resins are subsequently used to fabricate various plastic products. In all cases, the BP-6 serves solely as a fire retardant. The plastic manufacturers report that there are no by-products or waste streams associated with their processes for blending BP-6 into ABS (acrylonitrile-butadiene-styrene) resins.

One of the major consumers, Borg-Warner Corporation, recently reported[7] that it is now in the process of completely phasing out its use of Firemaster BP-6 and will soon start using substitute products.

CURRENT DOMESTIC USES FOR FIREMASTER BP-6[4/]

Industry	Approximate Allocation of Total Firemaster BP-6 Produced (%)	Examples
Business machines and industrial equipment	48	Typewriter, calculator and microfilm reader housings. Business machine housings.
Electrical	35	Radio and TV parts, thermostats, shaver and hand tool housings.
Fabricated products	12	Projector housings, movie equipment cases.
Transportation	1	Miscellaneous small automotive parts, i.e., electrical wire connectors, switch connectors, speaker grills.
Miscellaneous	4	Small parts for electrical applications, motor housings, components for industrial equipment.

A potential product of interest is a flame and moisture resistant material that contains PBB's, rubber, alumina, halogenated phthalic anhydride, and antimony trioxide, and can be used to impregnate fibrous-insulating materials (e.g., for cables or wires used in dishwashers and clothes dryers).[8] The company granted this patent has indicated that no wire or cable insulation is being produced by this method. Another potential use is disclosed in a patent covering the production of smoke retardant styrene polymers with octabromobiphenyl.[9] The company owning this patent has indicated that none of its ABS products has reached the commercial stage.[10] Polyurea shrink-resistant coatings for wool can be made flame resistant by addition of large quantities of hexabromobiphenyl.[11]

One former PBB producer has suggested that decabromobiphenyl can be used as a flame retardant for polyethylene, polypropylene, polycarbonates, polyester fibers, polyester resin, and polyamide fibers.[12] The same producer has indicated that hexabromobiphenyl can be used as a flame retardant for polyurethane foams and synthetic lattices.

Two of the most promising potential substitutes for PBB products are decabromobiphenyl oxide (DBBO) and a halogenated aliphatic compound. Both of these compounds currently sell at a significantly higher price than Firemaster BP-6. Both substitutes appear to be significantly less toxic than PBB's.

5. Environmental and health aspects of PBB's: Studies of biological effects of PBB's have been directed to three basic areas. First, acute toxicity has been investigated in several different animals. Second, studies have been made on the effects on animal reproduction. The third type of study has dealt with retention and paths for excretion of PBB's in various animals. The results to date indicate that PBB's have a low acute toxicity. PBB's have shown adverse effects on animal reproduction and a tendency to accumulate in fatty tissues. Adverse effects on organs (especially the liver) have also been attributed to these compounds.

III. CONCLUSIONS

The following conclusions, drawn on the basis of findings in this study, are arranged in the same general order as the sections of the study.

1. In November 1974, the only domestic commercial manufacturer of PBB's stopped production of these compounds.[13] At present (May 1975) no U.S. company produces these chemicals commercially, and it appears to be unlikely that domestic production will be resumed in the near future.

2. Data recently developed in a water pollution study by the Michigan Bureau of Water Management (for a plant which manufactures PBB's) indicates that some unidentified chemical production processes not related to direct production of PBB's can generate measurable quantities of PBB's in liquid waste streams. The exact cause of this PBB generation is unknown, but some potential PBB sources have been identified by MRI (Section V, p. 22).

3. The potential for water pollution by PBB's appears to be related primarily to production and formulation processes rather than to usage and disposal of plastic products containing these compounds.[14]

4. Domestic manufacturing sites at which PBB's are used as raw material for plastic formulations and manufacture of various thermoplastic products are potential sources of waste materials containing PBB's. Apparently none of these sites has been monitored for PBB's to date to determine any possible environmental pollution.[14]

5. The principal use of PBB's in the U.S. has been as a fire-retardant additive in thermoplastic products.[14] In these applications, the products do not come into contact with human food or clothing. There are no liquid applications for PBB's (Section VI, p. 32).

6. The present use of PBB's, solely from inventory supplies, is being phased out by the largest domestic consumer in favor of the use of substitute fire-retardant products which are less toxic.[7] The generally higher product prices for these substitutes are a deterrent to this transition.

7. Results of biological studies to date indicate that PBB's have a low acute toxicity (e.g., studies of acute oral toxicity show an acute LD_{50} of about 21.5 g/kg), can bioaccumulate in fatty tissues, and can cause adverse effects on animal organs, especially the liver (Section VII, p. 40).

IV. DISCUSSION OF METHODOLOGY

A study was made to develop information on the potential hazards to man and the environment associated with the production and use of the class of chemicals known as brominated biphenyls. A discussion of the major steps in the study follows.

A. Selection of Toxic Substances

The EPA task officer specified the class of chemicals known as brominated biphenyls as the subject for investigation. Polybrominated biphenyls (PBB's) are the only brominated biphenyls produced and used commercially to any significant extent, and the investigation was concentrated on them.

B. Identification of Production Sites and Volumes

1. Production sites: The domestic production sites for brominated biphenyls were identified using several standard reference publications, including the following:

* Chem Sources - USA, Directories Publishing Company, Inc., Flemington, New Jersey (1975).

* "Directory of Chemical Producers," Stanford Research Institute, Menlo Park, California, 1974 and 1975 editions.

* Chemical Week, 1973 Buyer's Guide Issue, McGraw Hill Publishing Company (1973).

In some cases, letter and telephone inquiries were made to confirm information derived from these reference publications.

2. Production capacity, production volumes, and imports: The available information of this type in the published literature was very meager. Most of these data were obtained by letter and telephone inquiries to specific chemical producers or distributors, trade organizations, and the U.S. Customs Bureau (Washington, D.C.).

C. Manufacturing Processes

Most of the information on domestic production technology for brominated biphenyls was obtained by a survey of the U.S. patent literature. A limited amount of data were obtained by telephone and written inquiries to chemical producers. A search of the chemical abstracts was made covering the period 1963 to 1974; very little useful information was found concerning commercial production methods for brominated biphenyls.

D. Waste Disposal Practices

The principal source of data on this subject was a copy of the waste discharge permit application submitted by Michigan Chemical Corporation to the Michigan Water Resources Commission. Michigan Chemical Corporation was selected as the source because this corporation was the sole U.S. producer of PBB's from 1973 until November 1974; at this latter date their PBB plant was shutdown indefinitely, and at present (May 1975) no domestic plant produces PBB's on a commercial basis.

Data furnished in this permit were used as the basis for a description and evaluation of waste disposal practices utilized in manufacturing operations.

E. Commercial Uses and Substitutes for PBB Products

Information concerning the existing and potential commercial uses for brominated biphenyl products and substitute products was acquired largely by telephone contacts with industry spokesmen.

F. Environmental and Health Aspects of PBB's

Data on physical and chemical properties, the environmental fate of products, and toxicity aspects were obtained from personal communications with producers and consumers and from published and unpublished technical literature.

V. PRODUCTION SITES AND VOLUMES

This section provides a brief synopsis of plant locations and production volumes for brominated biphenyl compounds. A list of individual plant sites and production volumes, together with annual gross production for the last 10 years, is presented.

A. Commercial Producers

During the last decade, only two domestic chemical companies produced brominated biphenyl compounds in commercial quantities. (Commercial production in the U.S. was started in 1970.) These companies and their PPB products are:

* Michigan Chemical Corporation (a subsidiary of Northwest Industries) at St. Louis, Michigan. Firemaster BP-6 is the only biphenyl derivative produced by this corporation. The major constituent in BP-6 is hexabromobiphenyl.

* White Chemical Corporation at Bayonne, New Jersey. Octabromobiphenyl and decabromobiphenyl have been produced by this corporation.

In May 1975, brominated biphenyls were not being produced on a commercial basis by any domestic manufacturers.

Production data for commercial PBB producers are shown in Table I. These data show that during the period of 1970 to 1975, Michigan Chemical produced a total of about 5,088,435 kg of Firemaster BP-6 and White Chemical Corporation produced about 45,350 kg of octabromobiphenyl plus decabromobiphenyl. The estimated total production of PBB's during this period is 5,133,785 kg (or 5,660 short tons). The available data indicate that PBB's were not produced domestically on a commercial basis prior to 1970. PBB's were not commercially produced in the U.S. from 1 January to June 1975 and it appears unlikely that any U.S. company will produce these chemicals during the period of 1975 to 1978 (MRI projection, based on private communications with former producers of PBB's).[4,5]

B. Suppliers of Laboratory Quantities

MRI identified nine domestic chemical suppliers who supply brominated biphenyls, and who have either produced or have imported laboratory quantities at certain periods during the last decade. Private communications with some of these suppliers indicate that the maximum production or importation of brominated biphenyls for each organization has been about 2 kg/year,

TABLE I

DOMESTIC PRODUCTION DATA FOR BROMINATED BIPHENYLS[4,5/]

Chemical Products	Producer and Location	Year	Production, Quantity (kg)	Comments
Firemaster BP-6 (Hexabromobiphenyl)	Michigan Chemical Corporation (a subsidiary of Northwest Industries), St. Louis, Michigan	1965-1970	None	
		1970	9,070	
		1971	90,703	
		1972	1,043,084	
		1973	1,768,707	
		1974	2,176,871	
		1975	None	MRI projection
		1976-1978	None	MRI projection
Octabromobiphenyl and Decabromobiphenyl	White Chemical Corporation Bayonne, New Jersey	1965-1970	None	
		1970-1973	45,350	
		1974	None	
		1975	None	MRI projection
		1976-1978	None	MRI projection
	Estimated total U.S. production	1965-1975	5,133,785	

and that the products are prepared only on a custom synthesis basis.[15,16] Thus, the total PBB quantity involved for these suppliers is considered to be negligible compared to the volume of domestic commercial producers. A list of these suppliers is shown in Table II.

TABLE II

DOMESTIC SUPPLIERS OF LABORATORY QUANTITIES OF BROMINATED BIPHENYLS[a]

Company	Location
Fine Organics	Lodi, New Jersey
Biochemical Laboratories, Inc.	Hawthorne, California
Eastern Chemical	Hauppage, New York
Chemical Samples Company	Columbus, Ohio
Columbia Organic Chemical Company	Columbia, South Carolina
K&K Laboratories	Plainview, New York
Fairfield Chemical Company	Blythewood, South Carolina
Ethyl Corporation	Baton Rouge, Louisiana
Research Organic/Inorganic Chemical Corporation	Belleville, New Jersey

a/ Companies which had a capability to produce kilogram quantities of brominated biphenyls during the last decade. Some of these companies apparently never produced these chemicals.

The available data indicate that there are no significant imports of brominated biphenyl compounds[17] (i.e., the total imports apparently amount to only kilogram quantities).

VI. MANUFACTURING METHODS, BY-PRODUCTS, AND CONTAMINATION RISKS

A. Introduction

The following discussion covers the basic process technology for commercial production of polybrominated biphenyls (PBB's), including potential sources of environmental contamination by PBB's. The first subsection discusses, in a general manner, the operating parameters that affect the production of these chemicals as by-products or wastes. The principal source of information on production technology was the U.S. patent literature. The second and third subsections describe the recent Michigan animal feed contamination incident and a study by the Michigan Bureau of Water Management of water pollution in the area of the Michigan Chemical Corporation plant at St. Louis, Michigan.

Until recently (see Section III), two domestic chemical companies, Michigan Chemical Corporation and White Chemical Corporation, produced commercial quantities of PBB's. No evidence was found of any current (1975) production of PBB's in the U.S. Spokesmen for these two companies have reported that the actual production processes used are proprietary; therefore, only general information was obtained from these sources concerning process technology. Michigan Chemical Corporation has indicated that there are no patents covering manufacture of their only PBB product, Firemaster BP-6. Information provided by a private communication[13] indicates that the by-product hydrogen bromide (HBr) formed during production of Firemaster BP-6 is contaminated with PBB's, and that much of this HBr is processed to recover bromine for use as a raw material in the same plant.

A description of production processes identified in the patent literature is given in the following subsection.

B. Manufacturing Methods Discussed in Patent Literature

The Dow Chemical Company was issued a patent in 1974 concerning, among other reactions, bromination of biphenyl with bromine chloride under pressure to produce a product containing five or six bromine atoms on each aromatic ring.[18] This process consists essentially of brominating biphenyl with bromine chloride (BrCl) in the presence of iron or a Friedel-Crafts catalyst in a closed vessel at or near autogenous pressure to obtain rapid polybromination of the aromatic nucleus. The reaction may suitably be conducted at about room temperature, and is completed in a few hours, with yields in excess of 80% generally being obtained.

Bromine chloride is prepared by mixing equal molar amounts of bromine and chlorine in a closed container; the bromine chloride thus formed is withdrawn from the liquid phase in the vessel.

Decabromobiphenyl, in addition to a lower polybrominated product, is prepared by adding a catalyst (aluminum chloride) and biphenyl to a batch reactor, and then slowly adding bromine chloride in 0 to 20% stoichiometric excess. For example, 10 to 12 moles of bromine chloride may be reacted with each mole of biphenyl.

As the bromine chloride reacts with biphenyl, the hydrogen chloride formed as by-product is retained in the reactor under essentially autogenous pressure. The pressure may range from 10 to 200 psig during the course of the reaction. The reaction temperature is not critical; the temperature may range from 10 to 150°C. A solvent, such as methylene chloride, may be used in the reaction, although good conversions and yields are obtained by using excess bromine chloride as the solvent. Best results are obtained when the reactor is operated under essentially anhydrous conditions; water apparently deactivates the catalyst. Essentially complete bromination is generally obtained within a few hours. After the reaction, the solid products are separated from the methylene chloride solvent. The advantages claimed for this process include high product yields, low yields of chlorinated compounds, short reaction periods, and efficient utilization of bromine.

A patent issued to the Ethyl Corporation in 1973 concerns an improved method for producing polybrominated aromatics.[19] This process involves reacting an aromatic compound with bromine in the presence of a halogenated catalyst and solvent quantities of methylene bromide at a temperature sufficient to sustain a rapid reaction rate. The invention is applicable to a large variety of aromatic compounds; however, biphenyl is the most preferred compound.

The preferred amounts of bromine utilized in this process are from 7 to about 9 moles of bromine per mole of biphenyl. The reaction of bromine with biphenyl is usually conducted in the liquid phase, and is initially exothermic. A preferred reaction temperature range is from room temperature to 100°C. The amount of catalyst required depends on the desired degree of bromination. The catalyst (aluminum chloride or aluminum bromide) is generally supplied to the reaction mixture in amounts of from 0.001 to 0.007 mole/mole of bromine. The use of solvent quantities of methylene bromide allows the reaction to proceed to the point of producing highly brominated biphenyl, without the product becoming a solid or agglomerating and preventing further bromination. Generally, sufficient solvent is required to maintain the reactants and brominated products in an adequate homogeneous reaction mixture. The preferred ratio of solvent to aromatic compound is about 10 or 15:1 (moles per mole). Although reaction time is not critical, the preferred reaction time is from about 2 to 10 hr. Hydrogen bromide is formed as a by-product.

The product consists of polybrominated biphenyl in the solvent with unreacted bromine and small amounts of catalyst and partially brominated biphenyl. When the desired degree of bromination is obtained, the reaction is stopped by cooling and successively washing the reaction mixture with acid, then alkali, and finally water. The organic portion of these washings is dried by adding sodium sulfate. The drying agent is removed by filtration and the solvent is stripped to recover a crude product. This product can be recrystallized from solvent or washed with solvent, followed by solvent stripping in an evaporator, depending upon the product purity required. Gas evolved during the reaction can be scrubbed with a caustic soda solution to remove noxious chemicals before being vented to the atmosphere. Example quantities of reactants, operating conditions, and results claimed for this patented process are summarized in Table III.

Chemische Fabrik Kalb G.m.b.H., Cologne-Kalk, Germany, obtained a U.S. patent in 1966 for a process of bromination of aromatic compounds, especially diphenyl, diphenyl ether, and mixtures thereof.[20] The bromination process is carried out at 20 to 65°C, using 1.01 to 1.2 g-atoms of bromine per gram-atom of hydrogen which is being substituted, and a quantity of chlorine which, at most, is equimolar with respect to the bromine. The products contain at least 4 atoms of bromine per mole of aromatic compound used as a raw material. Following completion of the bromination reaction, a quantity of an alkylene (e.g., ethylene or propylene) is added to the reaction mixture to bind the free bromine with the formation of the corresponding alkylene dibromide. A modification of the process involves the use of alkylene bromide as a solvent.

An example of the application of this process for preparation of brominated diphenyl is described in this patent. Diphenyl (308 parts by weight) was dissolved in 800 parts of ethylene bromide and 4 parts of iron powder are added thereto. Then, 1,430 parts of bromine and 632 parts of chlorine were introduced into the mixture with vigorous stirring over a period of about 2 hr. During the addition of bromine and chlorine, the temperature of the reaction mixture ranged from 20 to 60°C. After the bromination had been completed, the excess bromine contained in the reaction mixture was bound by adding ethylene to form ethylene dibromide. The pasty reaction mixture was filtered, and the ethylene dibromide obtained as filtrate was suitable for reuse as solvent. The filter cake was washed with ethanol and dried. The dried solid product contained 1,740 parts of octabromodiphenyl containing 80.9% of bromine and 1.5% of chlorine. This product yield was 93.5% of theoretical.

C. Description of the Michigan Animal Feed Contamination Incident

The recent accidental contamination of animal feed and livestock throughout Michigan with polybrominated biphenyl fire retardant stimulated a number of research studies, including an evaluation of the potential for water pollution from production of PBB's--as well as studies of the toxicity

TABLE III

BROMINATION OF BIPHENYL[19/]

Example No.	Reactants (Parts by Weight)					Conditions		Products			
	$(C_6H_5)_2$	Br_2	CH_2Br_2	Catalyst	Br_2 Equivalents[a/]	Time (hr)	Temp. (°C)	Weight (parts)	Avg. Br_2 Number[b/]	Weight Percent Br	Percent Yield Based on Avg. Br Number
1	17.8	122	197	0.88 $AlBr_3$	9.2	7.2	25-85	97.7	8.69	81.0	Quantitative
2	17.8	122	187	0.99 $AlBr_3$	9.2	4.3	25-98.5	98.2	8.75	80.3	Quantitative
3	17.8	157	200	1.12 $AlCl_3$	8.5	2.5	25-95	85.3	8.4	80.0	90.4
4	17.8	161	200	0.60 $AlCl_3$	8.75	3.0	25-95	95.0	8.41	79.4	Quantitative
5	17.8	169	250	0.38 $AlCl_3$	9.2	2.75	25-95	96.5	8.53	79.6	Quantitative
6	17.8	184	267.5	1.93 $AlCl_3$	10.0	4.0	25-95	95.5	8.85	81.6	97.4
7	17.8	175	250	0.99 $AlCl_3$	9.5	2.1	25-95	100.0	8.9	82.2	Quantitative

a/ Br_2 equivalents are number of Br atoms available for reaction with biphenyl from Br_2 charged; calculated by dividing moles of Br_2 by moles of $(C_6H_5)_2$.

b/ Average bromine number determined by VPC; certain peaks assumed to be hepta-, octa-, nona-, and decabromobiphenyl based on retention time. Area percent used for calculations.

and biological properties of this class of chemicals. Because of the public concern resulting from this contamination, a detailed description of the Michigan animal feed contamination incident is included here.

Some Michigan farm crops (e.g., corn silage) commonly used in the feed rations for dairy cattle have relatively low contents of magnesium--a desirable element in the feed. Therefore, it is a common practice in Michigan feed mills to supplement dairy cattle feed concentrates with purchased magnesium oxide powder.

The Michigan Chemical Corporation of St. Louis, Michigan, is one supplier of magnesium oxide feed supplement to cattle feed mills throughout Michigan and in some other states. This corporation also manufactures a number of other chemicals, including Firemaster BP-6, a fire retardant product containing a mixture of PBB's. Firemaster BP-6 is a powdery product similar in appearance to magnesium oxide powder.[3/]

For a number of years, magnesium oxide and Firemaster BP-6 were bagged by Michigan Chemical in labeled paper bags with distinctive colors. During the spring of 1973, however, a paper shortage developed and the bag supplier could no longer deliver both types; Michigan Chemical then began using the same type of colored bag for packaging its Firemaster BP-6 and magnesium oxide. Both materials were still being manufactured, bagged, and labeled correctly. Then during transfer of some of the filled bags to a company warehouse, a fork lift operator apparently failed to identify correctly his cargo, and bags of both types of products were accidentally stacked together in a storage area. When the Michigan Farm Bureau subsequently ordered magnesium oxide from Michigan Chemical, the shipment was made from the stacks of mixed products. After delivery to the Farm Bureau, the material was either used in local feed mills or shipped out to satellite mills for incorporation into cattle feed. This cattle feed was widely distributed and used by Michigan farmers. Subsequently, cross-contamination of other animal feeds with Firemaster BP-6 occurred in these mills and thus the contamination was spread to other farm animals.[21/]

Information on one Michigan dairy herd[22/] indicates that the contaminated feed supplement was incorporated into a pelleted feed product at the rate of 4 kg/MT. Thus, the maximum concentration of BP-6, which could have been present in the contaminated feed, was probably about 400 ppm.

This incident of accidental contamination of animal feeds resulted in several adverse environmental and health effects; some of these effects have not yet been fully identified and assessed.

A recent technical article reports on a syndrome of acute to chronic toxicosis associated with feed contamination in one Michigan dairy herd.[22] Clinical signs of PBB contamination in the cows included an initial marked decrease in milk production and feed consumption, followed by development of abscesses and hematomas. Liver lesions were one of the most commonly reported pathological changes, and the results indicated that PBB in the diet of cows can adversely effect their reproductive organs. Concentrations of PBB's in tissues from two cows that had consumed contaminated feed ranged from 84 ppm in kidney fat to 310 ppm in liver fat; the concentration in milk fat ranged from 43 to 56 ppm.[22]

Although cattle began getting sick in October 1973, PBB was not identified as the cause until April 1974.[3] Not all of the contaminated animals died or even got sick, but all suspect animals and their products were quarantined by state officials and could not be sold. In May 1974, more than 30 Michigan dairy herds were quarantined by the State Department of Agriculture, and the owners were unable to sell milk or meat or to dispose of dead animals from their farms. By July 1974, 92 food producing premises in Michigan were under quarantine; 44 of these involved cattle and the remainder involved poultry and swine. Starting in 1974, the FDA tested cheese, butter and condensed milk for brominated biphenyl residues.[1]

In June 1974, dairy cows and milk were being sampled in Ohio, Wisconsin, Georgia, Missouri, Indiana, Illinois, Iowa, Kentucky, and Michigan for violative PBB residues by the USDA and the FDA. The Agriculture Department found PBB residues as high as 100 ppm in cattle; the FDA sampled and tested milk using a guideline of 1 ppm of PBB.[2] Michigan Chemical Corporation reportedly has recalled all lots of magnesium oxide manufactured since March 1973 from eight states because of the risk that the shipments contained PBB. Also, the Farm Bureau service in Battle Creek, Michigan, is reported to have recalled its "24% Hi Moisture Corn and Silage Balancer No. 402" manufactured since March 1973, because the fire retardant was used as additive instead of feed supplement.[2]

In February 1975, a news article reported that many farm animals and food products contaminated with PBB had been destroyed and buried. The casualty list included 11,000 cattle, 2,000 hogs, 1.5 million chickens, 4.6 million eggs and small amounts of dried milk, cheese, and butter; also 683 MT of contaminated feed were buried.[3]

PBB has also found its way into the blood of farmers who were exposed to the contaminated animal feed. It has been reported that many of the blood samples taken in June 1974 from 211 people who had contact with the contaminated feed contained PBB.[3] More detailed tests, involving blood samples, physical examinations, and medical histories were underway in February 1975 on another 300 people. Half were exposed to the feed; the other half were controls who had no known contact with PBB. No evidence was found that PBB has caused sickness in any humans.

A number of related research investigations and studies have been conducted in the wake of this Michigan incident. For example, two technical papers on PBB's are scheduled to be presented in June 1975 at a conference in Columbia, Missouri.[23] Also, a technical paper, "The Distribution and Clearance of Polybrominated Biphenyls by Cows," is scheduled for presentation at a meeting of the American Dairy Science Association in Manhattan, Kansas, in June 1975.[24] The U.S. Food and Drug Administration was recently reported to be contracting with the Michigan State Department of Health, Bureau of Community Health in regard to an epidemiologic study of health effects associated with the consumption of milk, meat and other food contaminated with polybrominated biphenyl.[25]

D. Water Pollution Aspects of Polybrominated Biphenyl Production

The incident of accidental contamination of animal feed in Michigan stimulated an independent evaluation of the potential for water pollution from production of PBB by the Michigan Bureau of Water Management of the Department of Natural Resources. This Bureau has reported recently on a study of the water pollution aspects of PBB production.[14] This study covers an initial evaluation of contamination of the Pine River downstream from the Michigan Chemical Corporation plant at St. Louis, Michigan, where the entire U.S. production of PBB's is centered. This plant is situated near the bank of the river and waste effluent is discharged through several outfalls directly into the river. The PBB concentrations measured by the Bureau in various outfalls are presented in Section V (p. 22). A discussion of the major findings of this water pollution study is given in the following subsections.

1. Receiving water concentrations: Water samples were taken from the Pine River at points downstream from the Michigan Chemical Corporation St. Louis plant. The reported PBB concentrations ranged from 3.2 µg/liter at the impoundment 69 m downstream from the plant to 0.01 µg/liter about 12.8 km downstream. Concentrations of samples taken 19.3 and 32.2 km downstream were below the sensitivity level of 0.01 µg/liter.

2. Fish tissue analyses: Fish samples collected by gill netting and angling from the Pine River were analyzed for PBB's by either the U.S. Food and Drug Administration Laboratory in Washington, D.C., or the Michigan Department of Agriculture Laboratory in East Lansing, Michigan. Elevated PBB levels were reportedly found in Pine River fish ranging up to a maximum of 1.33 ppm in carp (whole fillets; wet weight) captured in the reservoir immediately below the Michigan Chemical plant. Carp captured 4.8 km downstream showed a concentration of 1.26 ppm, and measurable concentrations (0.09 ppm) were determined in carp sampled 12.9 km downstream. The reported concentrations of PBB's in bullheads were low at all stations. The study report states that the fish contamination appears to be limited to the Pine River.

3. Discussion of results of water pollution study: Michigan Chemical Corporation officials are reported to have indicated that residues detected in fish during the Bureau surveys do not accurately reflect current operations, but rather are a result of losses that occurred prior to improvements made in 1972 in the plant waste disposal systems. To test this hypothesis, the Bureau staff initiated a study of PBB uptake in caged fish held in the area of plant discharges and at stations upstream and downstream from the plant. Measurable PBB uptake in newly introduced fish would imply that plant discharge rates of PBB's were still contributing to the problem. In a recent telephone communication,[26] a Bureau representative stated that the results of these caged fish tests indicate that recent (1974) Michigan Chemical Corporation plant discharges have contributed significantly to the problem of PBB contamination in the environment.

The Bureau report indicates that PBB bioconcentration factors computed by comparing levels in fish to Pine River water concentrations are approximately 20,000 to 30,000. The fact that this compares closely to reported concentration factors for polychlorinated biphenyls (PCB's),[27,28] suggests that fish in the Pine River in 1974 were probably in equilibrium with the existing level of stream contamination.

The significance of reported PBB concentrations in Pine River fish is unknown. No studies have been reported on possible adverse effects on these local fish populations. According to the Bureau report, the U.S. Food and Drug Administration had no established tolerance level for PBB's in fish tissue for human consumption in October 1974; the FDA guideline for PBB's in meat and chickens at this time was 1.0 ppm on a fat basis. If this guideline were applied to fish, the carp tested in the St. Louis, Michigan, area of the Pine River near the discharge from the Michigan Chemical Corporation plant and at least 4.8 km downstream would exceed this value.

A spokesman for the Michigan Bureau of Water Management has reported that the potential for water pollution by PBB's appears to be primarily related to production and formulation processes rather than through usage and disposal of plastic products containing these compounds.[14] He also indicated that domestic manufacturing sites where PBB's are used as raw material for plastic formulations and manufacture of various thermoplastic products are potential sources of waste materials containing PBB's. Apparently, no monitoring of these plastic formulation and finishing plants has been conducted to date to investigate possible environmental pollution by PBB's.

VII. WASTE DISPOSAL PRACTICES IN MANUFACTURING OPERATIONS

A. Introduction

The PBB producers declined to provide MRI with specific information concerning waste disposal practices, since the production processes are proprietary.

The White Chemical Corporation at Bayonne, New Jersey, is reported to have produced PBB's from 1970 to 1973; this corporation then permanently shut down its PBB manufacturing facility because of the Michigan incident and the risks of environmental contamination created by the operations.[29] During this operating period, White Chemical accounted for only about 4% of the total domestic production of PBB's. For this reason, the waste disposal practices for this company were not investigated by MRI. A spokesman for the Michigan Chemical Corporation at St. Louis, Michigan, has reported that his company produced PBB's from 1970 to 20 November 1974; the manufacturing facility for these chemicals was shut down for an indefinite period on the latter date.[13] At the time of this shutdown, company officials were planning on future disposal of wastes from PBB operations by deep-well injection. In May 1975, a Michigan Chemical official indicated that the corporation planned to utilize the former PBB production facility for other products and would not resume production of PBB.[4]

The Michigan Chemical Corporation facility at St. Louis, Michigan, has been in operation since 1935; the plant had about 400 employees in 1970. The major raw material is brine pumped from wells which are 914 to 1,219 m deep. Salt (NaCl) and bromine are extracted from this brine; other important products which have been manufactured at this site include:

* Brominated pharmaceutical and industrial compounds including anhydrous hydrogen bromide and hydrobromic acid.
* Pharmaceutical and industrial intermediates.
* Magnesium compounds (MgO, $Mg(OH)_2$, $MgCO_3$).
* Agricultural chemicals (grain, fruit, and soil fumigants).
* Rare earth compounds and metals, and development compounds.
* Flame-retardant compounds.

  Firemaster PB-6 (a mixture of polybrominated biphenyls, with an average of 6 atoms of bromine per mole of biphenyl).

  Firemaster T23P and LV-T23P, tris(2,3-dibromopropyl) phosphate.

Firemaster T33P, tris(1,3-dichloropropyl) phosphate.

Firemaster BP4A, tetrabromobisphenol-A.

Firemaster PHT4, tetrabromophthalic anhydride.

The Michigan Water Resources Commission has issued a number of reports on wastewater surveys (conducted in 1967, 1970, and 1973) covering the Michigan Chemical Corporation facility (St. Louis, Michigan) discharges to the nearby Pine River. The purpose of these surveys was to determine the quality and quantity of wastewater being discharged by this plant to the Pine River. The reported data do not include PPB concentration levels.

B. Discussion of Waste Disposal Practices at Michigan Chemical Corporation Plant

In May 1975, the Permit Branch of EPA (Chicago, Illinois, office) provided MRI with copies of all permit applications data for waste discharge by the Michigan Chemical Corporation at St. Louis, Michigan.[6] These data have been used by MRI as the basis for a description and evaluation of the waste disposal practices utilized by this corporation. Data of special interest to this project, for four outfalls (discharge streams) selected from 25 outfalls listed in this permit information, are presented in Table IV. This table also includes related outfall sampling and chemical analyses data obtained from a report by the Michigan Bureau of Water Management.[14] Waste discharge flowsheets for each outfall are referenced in the table.

As shown in Table IV, four Michigan Chemical Corporation production units had measurable concentrations of PBB in their liquid waste outfalls in 1974. The PBB concentration in these outfalls during sampling periods in 1974, ranged from 0.1 μg/liter for Outfalls Nos. 005-006 to 104 μg/liter for Outfall No. 002. All outfalls discharge into the Pine River. A brief discussion of each plant outfall of interest is given in the following subsections.

1. Outfall 002: The manufacturing unit which has this outfall produces tetrabromophthalic anhydride (the principal product), hexabromobenzene, bromoacetic acid, and tetrabromobisphenol A.

As shown in Figure 1, Outfall 002 serves noncontact cooling water and product wash waters and final filtrate for the manufacturing operations. The waste stream is composed of wash liquor and filtrate from washing of product filter cake and cooling water from process reactors. Waste-abatement equipment includes a solids separator to clarify wash water, and practices include dilution, segregation, and storage of waste acid for by-product sale or disposal. A fume scrubber is operated using circulating acid to avoid water washing and the attendant problems. The outfall discharge rate is about 427,700 liters/day; the average pH is 1.2.

TABLE IV

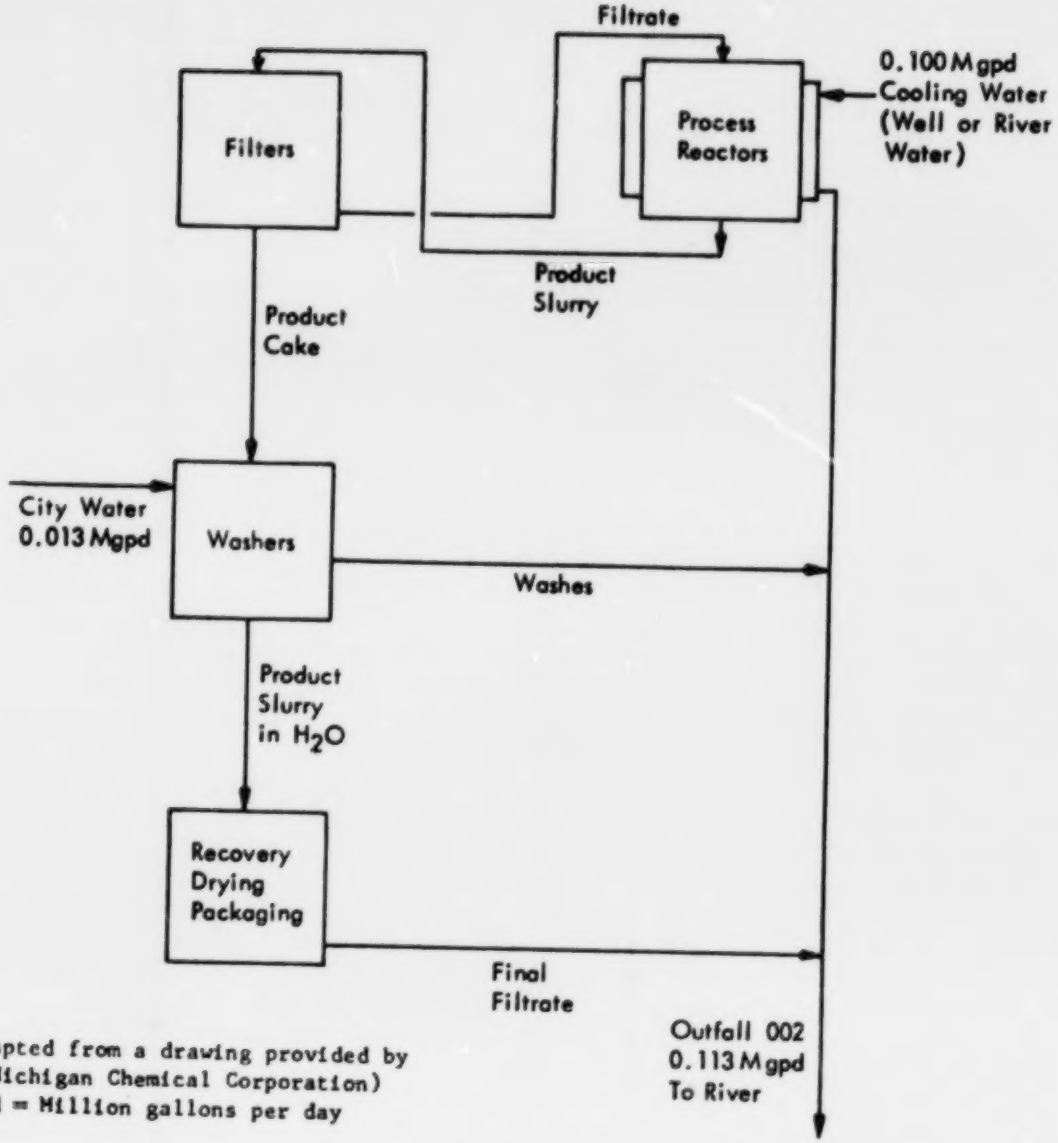
WASTE DISCHARGE DATA FOR MICHIGAN CHEMICAL CORPORATION MANUFACTURING FACILITY AT ST. LOUIS, MICHIGAN

Plant Waste Outfall No.	Manufacturing Activity or Process[a]	Waste Abatement Equipment and/or Practices[a]	Reference Waste Discharge Flowsheet Page No.	Reference Waste Discharge Flowsheet Fig. No.	Outfall Discharge Rate 10^6 liters/day[a]	Outfall Sampling and Evaluation[b] Sampling Date	PBB Concentration, µg/ℓ	Calculated PBB Discharge Rate, Based on Sample Data, Grams of PBB's/Day
002	Manufacture of industrial organic chemicals (SIC No. 2818) not otherwise classified. Production of brominated organic compounds including tetrabromophthalic anhydride, hexabromobenzene, bromoacetic acid, tetrabromobisphenol A.	Solids separator to clarify wash waters. Dilution, segregation, clarification, and storage of waste acid for by-product sale or disposal. Fume scrubber using circulating acid to avoid water washing and attendant problems.	25	1	0.4277 (0.113 gpd)	9/4-5/74	104	44.5
014	Manufacture of hydrogen bromide and hydrobrominated intermediates. Production of anhydrous hydrogen bromide (SIC No. 2813), hydrobromic acid solutions and zinc bromide (SIC No. 2819), and trimethylene chlorobromide, alkyl bromides, and bromotrichloromethane (SIC No. 2818).	Recovery of waste acid for re-use in other operations, collection of wastes for contract incineration.	27	2	1.6578 (0.438 gpd)	9/4-5/74	36	59.7
013	Manufacture of elemental bromine and organic derivatives. Tris, 2,3-dibromopropyl phosphate. Manufacture of elemental bromine (SIC No. 2819), methyl bromide, ethyl bromide, brominated flame-retardants, and other organic intermediates (SIC No. 2818).	Segregation and collection of certain wastes, surface condensers, special pumps, recovery and recycle, contract incineration, traps in outlet, use of spent brine in other processes.	28	3	1.6351 (0.432 gpd)	9/4-5/74	10	16.4
005[c]	Manufacture of industrial organic chemicals. Production of Hexabromobiphenyl. Discharge of cooling water, water used in area clean-up.	Segregation of waste acid, use of surface condensers to recycle materials, use of recovered by-product, use of chemicals producing minimum waste products. Traps to prevent spills from reaching drains and to skim off any accidental losses which do reach drain.	30	4	0.3066 (0.081 gpd)	[c]	[c]	
006[c]	Manufacture of industrial chemicals. Cooling water used in refrigeration plant. Refrigerated calcium chloride brine circulated to processes for coolant.	Well water used to cool refrigeration compressor coils is recirculated through system. Bleed off to river to maintain temperature. No contact with process materials.	30	4	0.5450 (0.144 gpd)	6/6/74 8/20/74 8/23/74 4/5/74 9/12/74 9/13/74	3.8 2.3, 3.6 0.1 6.6 5.5 3.1	2.07 1.61 0.05 3.60 3.00 1.69

a/ Based on data contained in waste discharge permit application filed with U.S. Army Corps of Engineers (Application No. MI-070-0X5-2-710319) at Detroit, Michigan, on 17 June 1971. Under the heading "Manufacturing Activity or Process;" the principal manufactured products are underlined.

b/ Based on data from a paper, "Water Pollution Aspects of Polybrominated Biphenyl Production: Results of Initial Surveys in the Pine River in Vicinity of St. Louis, Michigan," presented to the Governors Great Lakes Regional Interdisciplinary Pesticide Council on 17 October 1974 by John L. Hesse, Aquatic Biologist, Water Quality Appraisal Section, Michigan Bureau of Water Management, Department of Natural Resources.

c/ Outfalls Nos. 005 and 006 have been combined as one outfall by Michigan Chemical Corporation; at the time of outfall sampling and evaluation the 005 manufacturing facility was not in operation.



(Adapted from a drawing provided by
Michigan Chemical Corporation)
Mgpd = Million gallons per day

Figure 1 - Waste Discharge Flowsheet for Outfall 002--Michigan Chemical Corporation

A sample of this outfall had a PBB concentration of 104 µg/liter (1 µg/liter is equivalent to 1 part per billion (ppb)), the highest found in any of the four selected outfalls. This sampling and analysis study was conducted by the Michigan Bureau of Water Management in 1974. No information was found which explains the presence of PBB's in this outfall. An analysis by MRI shows that one potential source is PBB contamination of bromine raw material reclaimed from by-product HBr contaminated with PBB. Also, the coupling of molecules of partially brominated benzenes during the production of C_6Br_6 may be a source of PBB's. The possible presence of some biphenyl as an impurity in the chemical bisphenol A, used as raw material in the preparation of tetrabromobisphenol A, may be another source of PBB generation. Possible side reactions during the preparation of tetrabromobisphenol A and/or tetrabromophthalic anhydride appear to be less probable sources of PBB's in these manufacturing operations.

As shown in Table IV, the calculated daily PBB discharge rate for Outfall 002 (assuming that sampling data applies on a daily basis) is 44.5 g/day.

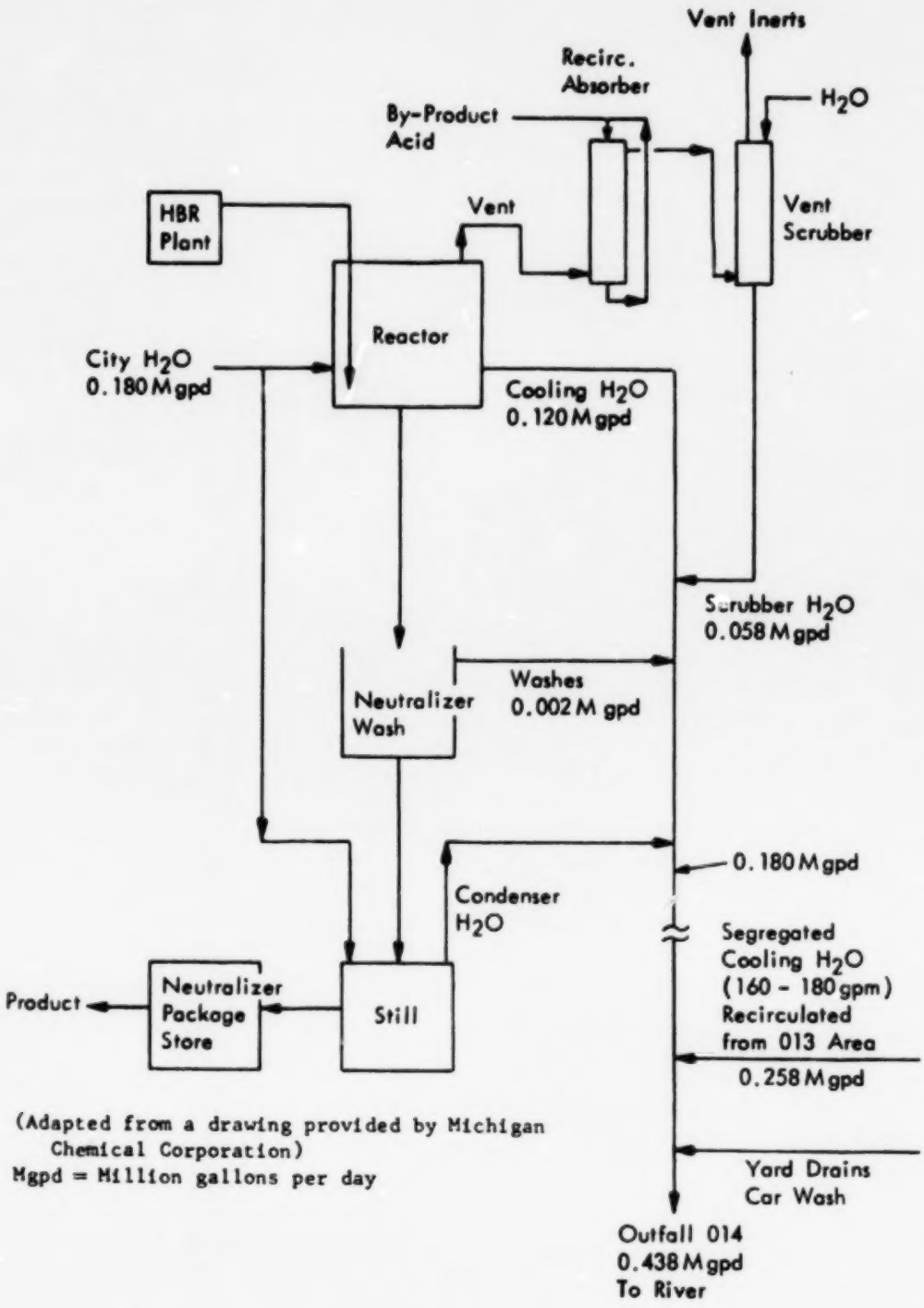
A planned improvement in the waste control system involves a collection dump for washes and transfer of the waste to a centralized sulfuric acid treatment system which will neutralize wastes. A company spokesman indicated in May 1975 that construction of this system was nearing completion.[30]

2. Outfall 014: This outfall services a multiple product area in which the principal products are anhydrous hydrogen bromide, trimethylene chlorobromide, and hydrobromic acid. Other products are listed in Table IV.

The liquid waste effluent contains city water used in this operation as shown in Figure 2, along with segregated cooling water, water from vent scrubbers, and product washes. Segregated cooling water from the 013 area (see Figure 3) is discharged to this outfall drain at some distance from the process area. Several yard drains also enter this sewer as it crosses the plant. Tank cars and trucks are washed near these drains. The outfall discharge rate is 1,657,830 liters/day and the average pH is 7.5.

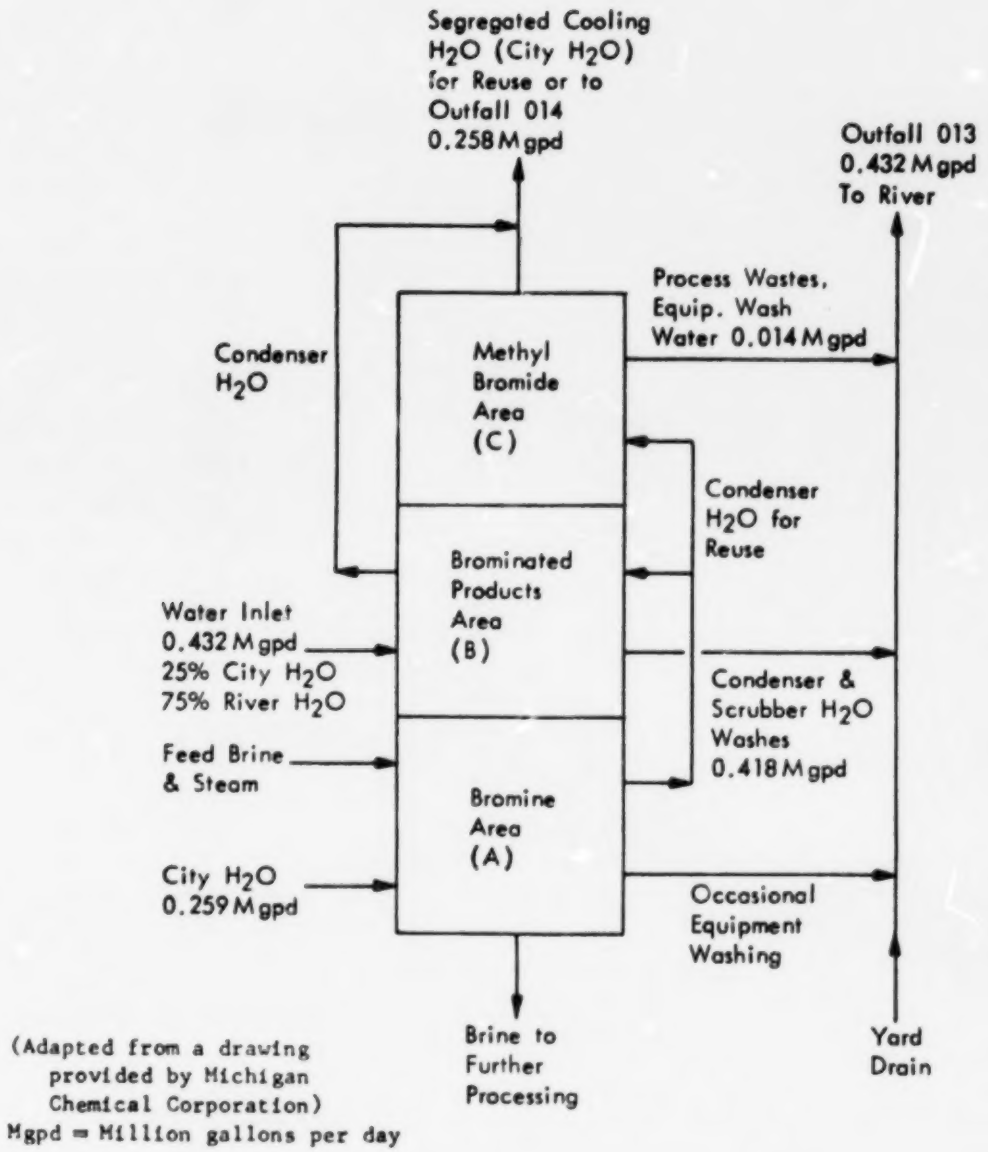
The reported waste-abatement practices include recovery of by-product acid and traps on the wash water to assure that no product is lost with the water. Plans call for collecting the washes for diversion to a brine disposal system (deep-well injection). Organic residues and wastes are segregated and sorted for pick-up by a waste contractor.

Analysis of a sample of this outfall, taken in September 1974 (Table IV), showed 36 µg/liter of PBB's. On a daily outfall basis, this concentration would result in a total discharge of 59.7 g of PBB's.



(Adapted from a drawing provided by Michigan Chemical Corporation)
Mgpd = Million gallons per day

Figure 2 - Waste Discharge Flowsheet for Outfall 014--Michigan Chemical Corporation



(Adapted from a drawing provided by Michigan Chemical Corporation)
Mgpd = Million gallons per day

Figure 3 - Waste Discharge Flowsheet for Outfall 013--Michigan Chemical Corporation

Potential sources of PBB's in this outfall include contaminated by-product HBr used in the absorber and feed material for the reactor (Figure 2).

3. Outfall 013: A multiple-product area producing bromine, brominated products and methyl bromide is serviced by this outfall, as shown in Figure 3. The principal products are elemental bromine and tris(2,3-dibromopropyl) phosphate. Cooling water (city water) from the bromine plant condensers is collected for reuse in other areas and discharged to Outfall 014.

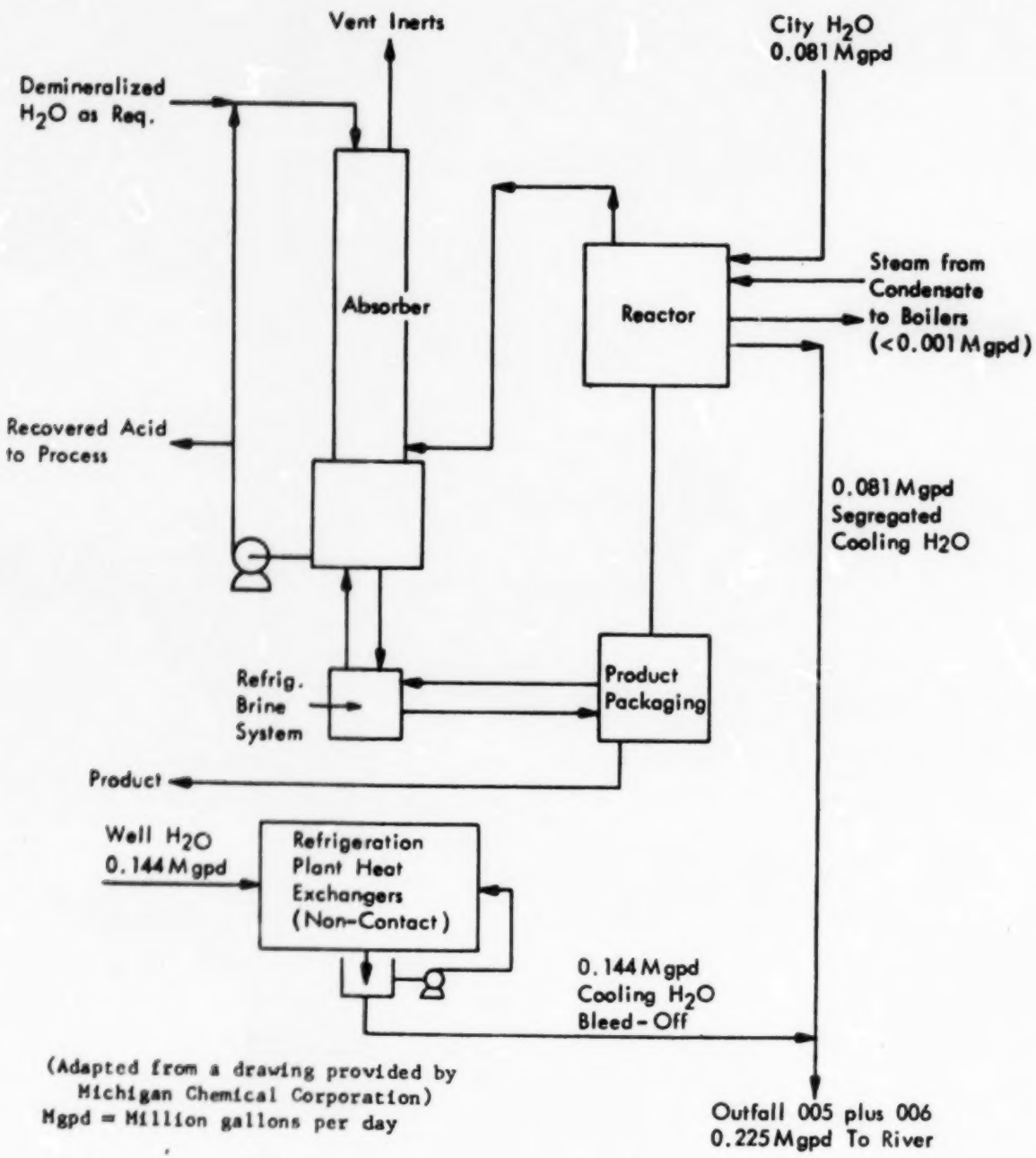
The brominated products area (B) uses a mixture of city water and river water for various purposes. Noncontact and contact cooling water, and off-gas scrubber water containing HCl from process vent gases and process washes, are all discharged together. Corporation plans call for installation of an HCl recovery absorber to control acidity.

Area (C) discharges segregated cooling water (reused city water) to Outfall 014. Small quantities of equipment wash water and condensate are discharged to Outfall 013 along with about 1,136 liters/day of sulfuric acid wastes. Michigan Chemical plans to treat these acid wastes in a central acid treatment plant.

The waste abatement practices described in the discharge permit application[6/] include segregation and collection of certain wastes, use of traps in the waste outlet, contract incineration of certain wastes, and use of spent brine in other processes.

The Outfall 013 discharge rate is 1,635,120 liters/day; the average pH is 3.8. Analysis of a sample of this outfall, taken in September 1974, showed a PBB concentration of 10 μg/liter (Table IV); this concentration corresponds to a daily discharge of 16.4 g of PBB in this outfall. A possible source of the PBB's in this outfall is the yard drain equipment wash water from operations involving bromination of various compounds.

4. Outfalls 005 and 006: As indicated in Table IV, these two outfalls have been combined by Michigan Chemical Corporation into one discharge stream. The 005 manufacturing facility produces industrial organic chemicals; the principal product is hexabromobiphenyl. The waste-abatement methods include segregation of waste acid and recovery of by-product HBr (containing PBB's as a contaminant[26/]) and use of surface condensers to recycle materials. Traps are used to prevent spills from reaching drains. Outfall 005 is reported to consist of segregated cooling water and steam condensate (see Figure 4). The specified discharge rate for the 005 outfall is 306,585 liters/day; the average pH of this discharge stream is 7.7. This facility was reported to have been shut down during the period (6 June to 13 September 1974) that outfalls were being sampled and monitored.[30/]



(Adapted from a drawing provided by
Michigan Chemical Corporation)
Mgpd = Million gallons per day

Figure 4 - Waste Discharge Flowsheet for Outfalls 005 and 006--
Michigan Chemical Corporation

The 006 facility involves primarily a refrigeration plant and the circulation of refrigerated calcium chloride brine (as a coolant) to various plant processes. Waste-abatement practices include the prevention of direct contact of the cooling water with process materials and recirculation of cooling waters.

Outfall 006 consists of well water recirculated over the refrigeration plant heat exchanger (see Figure 4). No treatment or process wastes are added to this water; at the time of the discharge permit application, Michigan Chemical had no plans for controls on this outfall. The specified discharge rate for this outfall is 545,040 liters/day and the average pH of this discharge is 7.8.

Chemical analysis of Outfall 006 samples taken between 6 June and 13 September 1974, by the Michigan Bureau of Water Management shows PBB concentrations ranging from 0.1 to 6.6 μg/liter. This range of concentrations is equivalent to a discharge of PBB's ranging from 0.05 to 3.6 g/day.

VIII. COMMERCIAL USES FOR PBB'S AND RELATED COMPOUNDS

A. Introduction

In recent years the immense loss of both lives and property to fires has led to demand by both governmental and nongovernmental organizations for improved fire-resistant materials.[31] Natural fibers have been relatively easy to treat with flame-retardant materials. However, flame retardant materials for synthetics have not been as easily developed. Some brominated organic compounds have been found to be more effective flame-retardants than chlorinated compounds for applications in plastic products.[32]

Polybrominated biphenyls have been some of the more promising flame retardants developed for synthetic materials. These materials have been able to meet the flame-resistance performance requirements, and are also economically feasible. They also have the desired property of having little effect upon the flexibility of the base compounds. For these reasons extensive interest has been shown in PBB's, especially hexabromobiphenyl (HBB), octabromobiphenyl (OBB), and decabromobiphenyl (DBB) as flame retardants.

The only PBB product to reach large scale commercial production is HBB, which is marketed as Firemaster BP-6 by Michigan Chemical Company. However, several other companies have shown an interest in the use of DBB and OBB, as well as HBB, as flame retardants. In this section, the actual uses of BP-6 are described, and some potential uses of PBB's are also discussed. The final few paragraphs of the section discuss some possible substitutes for PBB's as flame retardants.

B. Existing Uses

Little information was available concerning the use of Firemaster BP-6. The information gathered was of two basic types. First, Michigan Chemical Company supplied some information concerning the type of final products in which Firemaster BP-6 is used. Also, the two known domestic users of BP-6, Borg-Warner Corporation and Standard T Chemical Company, provided limited data concerning their use of this compound.

Information from Michigan Chemical Company indicates that BP-6 is used as a flame retardant for several thermoplastics. Use of BP-6 has been confined to those products which do not come into contact with food or feed and which are not used in fabrics subject to human exposure. The types of products in which BP-6 is used and the approximate percentage used in each application are listed in Table V.

TABLE V

DOMESTIC USES FOR FIREMASTER BP-6[33]

Industry	Approximate Allocation of Total Firemaster BP-6 Produced (%)	Examples
Business machines and industrial equipment	48	Typewriter, calculator and microfilm reader housings. Business machine housings.
Electrical	35	Radio and TV parts, thermostats, shaver and hand tool housings.
Fabricated products	12	Projector housings, movie equipment cases.
Transportation	1	Miscellaneous small automotive parts, i.e., electrical wire connectors, switch connectors, speaker grills.
Miscellaneous	4	Small parts for electrical applications, motor housings, components for industrial equipment.

After it was determined that BP-6 is the only commercial PBB, an attempt was made to identify and contact the users of BP-6. The only two companies that were identified are Standard T Chemical Company, Chicago, Illinois, and Borg-Warner Corporation, Parkersburg, West Virginia. Inquiries were made to these companies requesting data concerning quantities of BP-6 used and products in which BP-6 is used. The information obtained from these companies is summarized as follows.

Standard T Chemical Company uses BP-6 as a flame retardant as an ingredient in coating materials which have only an industrial use; they use an estimated 34,014 kg/year of BP-6 in their Staten Island, New York, plant.[34] Additional information concerning the products involved or the quantities of PBB's present in the product is considered by Standard T to be of a proprietary nature, and therefore, was not provided to MRI.[35] In response to questions concerning by-product and waste stream contamination with PBB's, Standard T reported that there are no by-products nor waste streams associated with their process.[35]

The major user of Firemaster BP-6 has been the Borg-Warner Corporation. The BP-6 is used to produce flame retardant ABS resin in three Borg-Warner plants: Parkersburg, West Virginia; Ottawa, Illinois; and Oxnard, California. ABS resins are produced by polymerizing acrylonitrile, butadiene, and styrene monomers. A Borg-Warner representative has indicated that his company used approximately 1,179,138 kg of Firemaster BP-6 during 1974.[36] This quantity accounts for about 55% of the total BP-6 produced that year.

The process in which BP-6 is used is reported to be a dry mixing process with no by-products or waste streams. The technical literature[37] indicates that a typical concentration of BP-6 in the final mixture is about 20% by weight. Lower BP-6 concentrations (e.g., 7 or 13%) are used in plastic formulations which include other flame-retardant additives.[37] The two components are mixed in a Banbury mixer (batch charge of about 136 kg) until the flux point of the ABS resin is reached and the flakes of BP-6 are melted. The mixture is then cooled and pelletized. During the cooling process, the impregnated ABS resin comes into contact with cooling water. However, a spokesman for Borg-Warner has reported that ABS is not water soluble and that PBB's are not transferred to this water. Substantiating data were not supplied, however.

A Borg-Warner representative has also indicated that flame-retardant ABS produced by his company is processed in the same manner as general ABS compounds.[36] ABS compounds generally may be used in any of several different processing steps. The two general categories of ABS products are injection molded and extrusion grade. Injection molding, extruding and calendering of ABS by a wide variety of techniques are possible. Both screw and ram injection molding can be used. It is also possible to electroplate ABS, and the resins can also be foamed by several techniques.[31] Thus, there are several commercial processes in which the BP-6 could possibly be introduced into the environment during secondary production stages. However, the available data are insufficient to establish the amounts of such possible environmental contamination.

In summary, two users of PBB's have been located who, together, consume approximately 56% of the annual production. Data from these companies, as well as from Michigan Chemical, indicate that the final disposition of the PBB's is in products which do not come into contact with food, feed, or human wearing apparel. It has also been reported that in the primary processing stage, there are no waste streams or by-products. However, no data have been obtained detailing the fate of the PBB's at the fabricating stage of the ABS.

Data are particularly needed on any PBB levels in cooling waters used during pelletizing of the ABS resins, and in other ABS products that are fabricated in the same equipment as flame-resistant ABS--since cross-contamination could occur.

C. Potential Uses

Three information sources were utilized to determine potential uses of PBB's. First, a search of U.S. patent literature was conducted, and all patents claiming the use of PBB's were obtained. A general literature search was also conducted to find any technical articles detailing uses of PBB's. Finally, the technical brochures of PBB manufacturers were examined to determine the recommended uses of their products.

In examining these sources, the only commercial use found for PBB's was as a flame retardant. However, there are several types of materials for which PBB's can be used as a flame retardant, and these are discussed in the following paragraphs.

A search of U.S. patents revealed six patents claiming PBB's as flame retardants. Five of these patents were issued to U.S. firms and one was issued to a German firm. Each U.S. firm was contacted to determine present production status under their patent. The following paragraphs detail the process and materials involved in each patent as well as information concerning present production status. While most of the patents discuss several alternative flame retardants, this discussion is concerned with those sections of the patents detailing the use of brominated biphenyls.

One patent studied by MRI involves a combination of phosphonium bromides and brominated biphenyls which can be used as a flame retardant for olefin polymers.[38] The specific phosphorus compound is a phosphonium bromide having either the formula $[R_3PR']^+Br^-$ where R is a phenyl or 2-cyanoethyl and R' is a lower alkyl or 2-cyanoethyl, or the formula $[R_3P\text{-}CH\text{-}CH\text{-}PR_3]^{++}2Br^-$ where R is defined as above. The specific brominated compound is decabromodiphenyl (DBB), octabromobiphenyl (OBB), hexabromobiphenyl (HBB), or tetrabromodiphenyl (TBB).

The patent indicates that the flame retardant should consist of a mixture of phosphonium bromide and brominated biphenyl ranging from a ratio of 2:1 to 1:2, respectively. This mixture should be incorporated into a polymer in amounts from 0 to 25% by weight, based upon the weight of the polymer. The flame retardant may be added to the polymer as a combination or as individual components in any of the following manners: (a) by milling the polymer and components on a two-roll mill in a Banbury mixer, etc.; (b) by molding the components and the polymer simultaneously; (c) by extruding the polymer and components; or (d) by blending all the materials together in a liquid or powder form and later forming the desired end-product. Also, the flame retardant may be incorporated during production of the polymer. Information obtained from contact with the company assigned this patent indicates that products are not being manufactured under this patent.[39]

Another patent is of a broad nature and identifies many specific components both for the flame retardant and for the base plastic. The general formulation consists of a thermoplastic compound for the base and a flame retardant comprising a polychloro-substituted organic compound, a polybromo-substituted organic compound, and if so desired, an antimony-containing compound or a tin-containing compound.[40] The specific brominated biphenyl mentioned in this Universal Oil Products Company patent is hexabromobiphenyl. The invention consists of an embodiment of the polychloro-substituted compound and hexabromobiphenyl, in combination, in the final composition in the range of 5 to 50% by weight of the finished product, the antimony-containing or tin-containing substitute in the range of 0.2 to 15%, and the thermoplastic substance in amounts ranging from 50 to 94.8% by weight. These materials may be combined by any mode of admixing known in the art. Universal Oil Products is not presently producing flame-retardant compositions using HBB, nor does it have any plans to produce such compounds.[41]

A patent assigned to Cities Service Company includes PBB's as a part of a mixture yielding nondrip, self-extinguishing polyethylene.[42] The general formulation consists of polyethylene, a halogenated organic flame retardant, ammonium sulfate or ammonium fluoborate, a metal compound synergist, such as antimony trioxide, and silica. The particular PBB's involved are decabromobiphenyl (DBB), octabromobiphenyl (OBB), and hexabromobiphenyl (HBB). The polyethylene is combined with the flame retardant so as to constitute 55 to 70% by weight of the final product. This is combined with 2 to 10% by weight of PBB, 5 to 10% by weight of ammonium sulfate or ammonium fluoborate, 5 to 10% by weight of a metal compound synergist, and 15 to 25% by weight of silica to obtain the final composition. These mixtures may be combined by any suitable technique known in the industry. However, they are usually prepared by mixing the flame retardant compounds with molten polyethylene. A Cities Service representative has indicated that PBB's are not used presently, and that there are no plans to use PBB's.[43] All products now being manufactured under this patent use brominated aliphatic flame retardants.

In November of 1973, General Electric was issued a patent for the production of a flame and moisture resistant material that can be used to impregnate fibrous-insulating materials.[8] The impregnating composition contains halogenated rubber, halogenated polyphenyl, hydrated alumina, halogenated phthalic anhydride, and antimony trioxide. The halogenated polyphenyls of interest are tetrabromobiphenyl, hexabromobiphenyl, and octabromobiphenyl.

The composition of the impregnating materials, in parts by weight, are:

Halogenated rubber	15-25
Polybrominated biphenyl	25-35
Hydrated alumina	30-40
Halogenated phthalic anhydride	3-9
Antimony trioxide	3-9
Phosphate ester	0-9
Aluminum stearate	0-1

The ingredients are dispersed in a volatile liquid organic such as toluene or xylene to aid in the preparation of the impregnating composition and its later application into the fibrous materials. First, the soluble halogenated rubber and PBB are dissolved, followed by the other soluble components. The insoluble components such as antimony trioxide, phthalic anhydride, and hydrated alumina are then slurried through the liquid by ball rolling into the rubber-biphenyl solution. The composition is then diluted with additional solvent until concentrations of about 25 to 200 parts by weight of solvent to 100 parts by weight of the flame-retardant components are reached. For the impregnating of asbestos and other inorganic fibers, 75 to 175 parts by weight of solvent to 100 parts by weight of flame retardant are preferred.

The invention also describes the flame-resistant, moisture-resistant insulation for wire and cable that can be produced from this flame retardant. The wire is said to have applications in high-temperature, high-moisture appliances such as dishwashers and clothes dryers. General Electric has indicated that no wiring is being produced under this patent with brominated biphenyl as a flame-retardant.[44/]

In October of 1973, Monsanto Research Corporation was issued a patent involving the production of smoke-retardant styrene polymers.[9/] The patent is basically concerned with the addition of iron, manganese or chromium 8-hydroxyquinolate to styrene polymers. However, one of the claims of the patent involves the addition of octabromobiphenyl (OBB) as a flame retardant. The specific embodiments described in the patent consist of ABS resin combined with 2%.4% by weight OBB and $Fe(8\text{-hq})_3$ ranging from 4.4 to 21.9% by weight. The patent did not describe the method by which the ingredients were combined. A representative from Monsanto has indicated that none of its flame-retardant ABS products has reached the commercial stage.[10/] He also indicated that Monsanto would probably not use PBB's in its products.

Another patent of interest is assigned to Chemische Fabrik Kalb G.m.b.H. of Cologne-Kalb, Germany.[45] This patent describes both the production and use of a flame retardant which is a mixture of brominated biphenyl and brominated biphenyl ether. The preferred product is obtained by brominating a mixture of 26.5% by weight biphenyl and 73.5% by weight biphenyl ether to a product containing 70 to 85% by weight of bromine. The patent describes the use of the above product as a flame retardant for a number of plastic resins. The flame retardant is used in quantities which provide a bromine content between 5 and 15% by weight in the synthetic resin. It is also advantageous to incorporate 3 to 15% by weight of antimony trioxide. The flame retardant can be added to the resin in several manners. First, it may be added to the monomer before polymerization. Also, the addition of the flame retardant to polyolefins may be accomplished during their production. Finally, the flame retardant may be admixed during the rolling, calendering, or extrusion of the polymers. The status of production of flame-retardant polymers under this patent was not determined.

An examination of the literature revealed only one additional use of PBB's as a flame retardant. Fincher et al.,[11] found that polyurea shrink-resistant coatings for wool could be made flame resistant by the addition of large quantities of hexabromobiphenyl. The flame resistant coatings were fast to repeated washings, but were not able to maintain the flame resistance properties after dry cleaning. The article is of Australian origin, and no information was obtained concerning the commercial application of this process.

Information was obtained from White Chemical detailing the chemical properties and suggested uses of their brominated biphenyls. They suggested that decabromobiphenyl can be used as a flame retardant for ABS, polystyrene, polyethylene, polypropylene, polycarbonates, polyester fibers, polyester resin and polyamide fibers.[12] Hexabromobiphenyl was suggested as a flame retardant for polyurethane foams and synthetic latices.

In summary, all information obtained indicates that the major potential uses for PBB's are as flame retardants for a variety of materials, principally various synthetic thermoplastics. However, some data indicate that PBB's can also be used in flame-retardant combinations for both wool and inorganic fibers. There is no information that suggests any use for PBB's other than as a flame-retarding agent.

D. Brominated Substitutes for PBB's

Because of public concern stimulated by the PBB contamination incident in Michigan, commercial producers and consumers of flame-retardants have become interested in the development and use of substitutes for PBB's. A brief discussion of potential substitutes is presented here.

The field of flame retardant additives for thermoplastic materials is in a rapidly developing stage. Several products have been developed and are being marketed which have flame-retardant properties similar to those of PBB's. However, these flame retardants are not as economical as PBB's. Several of these possible substitutes are described in the current technical literature.46/

Two of the most promising are decabromobiphenyl oxide, produced by Dow Chemical Company, Fine Organics, and Great Lakes Chemical, and a halogenated aliphatic produced by Cities Service Company. Both of these compounds are currently priced at about $3.86/kg ($1.75/lb),46/ which is significantly higher than the price of BP-6 (about $1.65/kg or $0.75/lb).

Decabromobiphenyl oxide (DBBO) is a compound similar in structure to decabromobiphenyl. The difference is that it has an oxygen atom which binds the two benzene rings. The toxicity of DBBO was studied in a Dow report mentioned in Section VII, p. 40; DBBO appears to be a much less toxic material than PBB's. However, according to Dr. Joseph Green of Cities Service Company, DBBO has a tendency to degrade to lower brominated biphenyl oxides. These lower order compounds may possibly pose environmental problems similar to those of the lower brominated PBB's.43/

The Cities Service product, Citrex BC-26, is a halogenated organic containing 29% bromine and 40% chlorine.46/ According to Dr. Joseph Green of Cities Service Company, this product is less toxic than PBB's and does not exhibit the property of bioaccumulation.43/

These and several other compounds have been developed which have flame-retardant properties equivalent to those of PBB's. However, the problem remains to develop compounds with these properties that have the same economic advantages.

IX. HEALTH AND ENVIRONMENTAL ASPECTS

A. Introduction

In the late 1960's several companies began to have an interest in polybrominated biphenyls (PBB's) because of their flame retardant capabilities. However, because of the similarity of these compounds to PCB's, there was some concern about the toxicity of PBB's. This concern, which was intensified by the Michigan cattle-feeding incident of 1973, has led to several extensive studies of the toxicological and environmental effects of PBB's.

The following subsections briefly discuss the findings of these studies under the separate headings of health aspects and environmental aspects. The health studies are directed to three basic areas: toxicity to animals, effects on animal reproduction, and animal retention and excretion of PBB's. The subsection on environmental aspects discusses physical and chemical properties of PBB's, and the fate of Firemaster BP-6 in the environment.

B. Health Aspects

1. Toxicity of PBB's: Since 1970, several chemical firms have sponsored studies of the toxicological effects of PBB's. The four major reports to date are of the Michigan Chemical Company study conducted by Hill Top Research Institute, Inc.,[47] the Dow study conducted by Norris et al.,[48] and two Du Pont studies conducted by Aftosmis et al.[49,50]

Each of these studies covered acute oral toxicity in rats and skin and eye irritation in rabbits. In addition, both Aftosmis et al. and Hill Top conducted inhalation studies on rats. Norris et al. also conducted 30 day and 2 year rat feeding studies, and Aftosmis et al.[49] conducted a subacute 28 day feeding study.

In all studies of acute oral toxicity, the test sample was administered by intragastric intubation to the rats. Both Norris and Aftosmis used a maximum dosage of 2,000 mg/kg[48,49] and found no signs of acute toxicity. The Hill Top study used higher concentrations and found the acute LD_{50} to be in the range of 21.5 g/kg.[47] The Hill Top study also indicated that some of the rats exhibited signs of systematic toxicity such as diarrhea stains, urine stains and emaciation at a 10 g/kg level.

To test dermal absorption toxicity, Aftosmis et al.[50] applied a paste containing either hexabromobiphenyl (HBB) or octabromobiphenyl (OBB) to the stomachs of rabbits for 24 hr and then removed it. The rabbits were then observed for 14 days. Hill Top Research[47] used the same procedure using only HBB. Both sets of data indicate that the acute dermal LD_{50} of HBB in rabbits is in the range of 2.15 to 10 g/kg.[47,50] Aftosmis et al. also noted significant liver enlargement at dosage levels of 1.0 g/kg and larger, and Hill Top noted ataxia and emaciation in the majority of rabbits at all dosage levels after the first five post exposure days.

The skin and eye irritation studies on rabbits conducted by all three groups indicated only slight irritation. This slight irritation disappeared quickly after the removal of the PBB-treated skin patches. Aftosmis et al.[50] also found no evidence of irritation on 173 human volunteers who wore a polyester fabric sample containing 6% by weight OBB.

To test acute inhalation toxicity, Hill Top Research exposed 10 rats to HBB at a concentration of 71.1 mg/liter for 1 hr.[47] Although no rats died, emaciation was noted in the majority of rats on the fourth postexposure day and persisted in six rats until termination. The rats showed an average weight loss of 59 g and, upon termination, showed depleted body fat stores. In their inhalation study, Aftosmis et al. found that rats exposed to PBB's at levels of 13.0 and 18.4 μg/liter for 4 hr showed a significant increased liver to body weight ratios.[50] Additional tests indicated that the threshold level for this liver enlargement is about 2.6 μg/liter.[50]

Both Norris et al. and Aftosmis et al. fed rats OBB at dietary levels ranging from 0 to 1% for approximately 1 month. Both found liver weight increases at feeding levels of 0.01% and above. Aftosmis also found a buildup of bromine in the fat, liver and muscles of rats fed at the 100 ppm level and above. The bromine level in the fat had not decreased 18 weeks after the feeding ended.

Although all three studies indicate a low acute toxicity for PBB's, both Aftosmis et al. and Norris et al. recommend that these compounds not be used as flame retardants because of the PBB accumulation in the liver and in body fat.

2. Effects of PBB's on animal reproduction: Four studies have been conducted which examine the effect of PBB's on the reproductive process. Aftosmis et al.[49] have studied the embryotoxicity of PBB's in rats. Cecil et al.[51,52] and Lillie et al.[53] have conducted studies on laying hens which examine the effects of PBB's on egg production, fertility and hatchability.

Aftosmis et al. administered OBB in the diet of rats at levels of 0, 100, 1,000, and 10,000 ppm from the 6th through the 15th day of the gestation period.[49] The pups were delivered by caesarean section on the 20th day of pregnancy. Neither the outcome of the pregnancy nor the embryonal development was effected by treatment. However, four fetuses, one from each of four

different litters, showed major abnormalities. These abnormalities were found in two litters each at the 1,000 and 10,000 ppm levels. Further studies would be required to determine whether these abnormalities were related, or whether they were a chance occurrence.

In two studies primarily concerned with the effect of PCB's on laying hens, Cecil et al.[51,52] also examined the effects of Firemaster BP-6 (hexabromobiphenyl) on hens. Both studies indicate that a level of 20 ppm of HBB in feed has no effect on the hatchability or fertility of eggs. However, it was found during the 2nd month of feeding that egg production was 11.5% less than that for the control birds.[51] These findings were substantiated by Lillie et al.[53]

Data from the Michigan contamination incident indicate that the PBB in the diet of cows tends to have a dramatic effect upon their reproduction processes.[22] Thus, there are data which indicate that PBB's in the food intake can have an adverse effect on the reproductive process of various animals.

3. Retention and excretion of PBB's: Several studies have been undertaken to determine the path of PBB's in animals' systems. G. F. Fries et al. studied the retention and excretion of PBB's in both hens and cows,[54] and G. F. Fries and G. S. Morrow later studied the excretion of PBB's in the milk of cows.[55] Norris et al. conducted ^{14}C metabolism studies on OBB in rats.

In their study of hens, G. F. Fries et al. fed a group of 35 hens a diet containing 20 ppm PBB for 7 weeks.[54] At the end of a 9-week period, the PBB levels in hens sacrificed were 21.5 ppm in the eggs and 69.5 ppm in body fat. After 16 weeks the level had dropped to 2.2 ppm in eggs, but the level in body fat had dropped only to 62.4 ppm. Fries et al. also found a significantly higher retention of hexabromobiphenyl than heptabromobiphenyl in the body fat of the chickens. It should also be noted that 45% of the PBB residue was excreted through the eggs. As part of the same study, Fries et al. incorporated excreta from the hens into the diet of a cow to give PBB levels of 0.61 ppm in the cow's diet. After 30 days, a steady state of about 6 ppm was reached in the milk fat of the cow.[54] After the PBB feeding was stopped, the concentration fell about 80% in the first 10 days, and more slowly thereafter.

In a later study, G. F. Fries and G. S. Morrow fed four cows 10 mg/day of PPB for 60 days.[55] After 30 days the PBB level in the milk fat plateaued at 3.07 ppm. After the PBB feeding was stopped, the level declined 71% in the first 15 days. The decline then slowed drastically with a half-life of 58 days

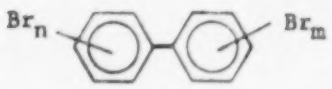
In the ^{14}C metabolism study conducted by Norris et al., rats were dosed with 1 mg of OBB and then were tested at 24-hr intervals for 16 days.[48] Approximately 62% of the ^{14}C activity was found in the feces at the end of 24 hr. However, after the 16th day about 26% of the ^{14}C activity had not been recovered. When the rats were sacrificed on the 16th day, ^{14}C activity was found in the adrenal, heart, adipose, skin, liver, and pancreas tissue.

C. Environmental Aspects

During 1970 to 1975, Firemaster BP-6 has been the principal PBB flame-retardant material produced and sold domestically. The following subsections discuss the properties of BP-6 and decabromobiphenyl and the fate of BP-6 in the environment.

1. Physical and chemical properties of Firemaster BP-6

General structure and composition



$n + m = 6$

BP 6 is a mixture of brominated biphenyls with an average bromine content equivalent to about six bromine atoms/biphenyl molecule. This product is a mixture of the following brominated biphenyls.[33]

	%		%
Tetrabromobiphenyl	2.0	Heptabromobiphenyl	13.8
Pentabromobiphenyl	10.6	Other bromobiphenyls	11.4
Hexabromobiphenyl	62.8		

Bromine content	75%
Softening point	72°C
Density	2.57 g/ml at 26°C

Vapor pressure, mm of Hg

90°C	7.6×10^{-5}
140°C	7.6×10^{-3}
220°C	7.6×10^{-1}

Solubility at 28°C, g/100 g solvent

Dioxane	115
Toluene	97
Styrene	78
Benzene	75
Chloroform	40
Carbon tetrachloride	30
Dimethyl formamide	16
Ethyl acetate	8
Acetone	6
Petroleum ether	2

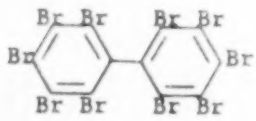
Water solubility, 25°C — 11 parts per billion

Thermal stability — Decomposes at 300 to 400°C

Chemical and photolytic stability: Firemaster BP-6 is relatively inert chemically. Although no data are available on the photolytic stability of Firemaster BP-6, a study of the photolytic stability of octabromobiphenyl indicates ultraviolet light readily degrades this material under conditions where polychlorinated biphenyls (PCB's) are not. Similar behavior of BP-6 would be expected. This photolability is expected since the aromatic C-Br (71 kcal/mole) bond is weaker than the C-Cl (85.6 kcal/mole) bond.

2. The structure and properties of decabromobiphenyl

Structure



General properties

Color	White to off-white powder
Percent Br (theoretical)	84.7
Molecular weight	944

Volatility (by TGA)	Less than 5%	341°C
	10%	363°C
	25%	388°C
Melting point (°C)	380 to 386	

3. The fate of Firemaster BP-6 in the environment: Information concerning the probable fate of BP-6 in the environment has been provided by the manufacturer.[33/] Based on their knowledge of the end-use products into which Firemaster BP-6 is incorporated, it is assumed that the major portion of these products (which have a useful life of 5 to 10 years) end up in a junk pile or are buried in a sanitary landfill. The ultimate disposition of BP-6 upon burial is uncertain. In their opinion, BP-6 eventually undergoes oxidative/biological degradation forming carbon dioxide, water, and bromide ion. When a chemical change in the BP-6 molecule does occur, degradation proceeds relatively rapidly.

Although no data on soil migration of BP-6 are available, a Michigan Chemical spokesman believes that migration is minimal. This opinion is based on two factors: (a) BP-6 is known to be tightly bound into the plastic into which it is incorporated; and (b) a Monsanto study on polychlorinated biphenyl migration in soil indicates that such compounds, especially the highly chlorinated biphenyls, exhibit an extremely small migration tendency. Since BP-6 should exhibit properties similar to the higher polychlorinated biphenyls, BP-6 does not seem to be easily leached from the soil.

REFERENCES

1. Pesticide Chemical News, p. 8, 5 June 1974.

2. Pesticide Chemical News, p. 9, 19 June 1974.

3. Chemical and Engineering News, p. 7, 24 February 1975.

4. Personal Communication with Dr. Fred Kerst, Vice President, Michigan Chemical Corporation, St. Louis, Michigan, May 1975.

5. Personal Communication with Mr. James Dunphy, White Chemical Corporation, Bayonne, New Jersey, May 1975.

6. U.S. Department of the Army, Corps of Engineers, Application for Permit to Discharge in Navigable Waters, Application M1-070-0X5-2-710319, Filed on 17 June 1971, by Michigan Chemical Corporation, St. Louis, Michigan.

7. Personal Communication with Mr. James Spainhower, Borg-Warner Corporation, Parkersburg, West Virginia, 19 May 1975.

8. Nicodemus, P. O., and H. L. Wilson, "Flame and Moisture Resisting Impregnating Compositions for Fibrous Materials and Products Thereof," U.S. Patent 3,772,455, assigned to General Electric Company, Patented 13 November 1973.

9. Parts, L. P., and J. T. Miller, "Smoke Retardant Styrene Polymer Compositions," U.S. Patent 3,766,157, assigned to Monsanto Research Corporation, Patented 16 October 1973.

10. Personal Communication with Mr. Wetzel, Monsanto Research Corporation, St. Louis, Missouri, 14 May 1975.

11. Fincher, K. W., G. B. Guise, and M. A. White, "Machine-Washable Flame-Resistant Wool," Textile Res. J., pp. 623-625, October 1973.

12. Personal Communication with Mr. James Dunphy, White Chemical Company, Bayonne, New Jersey, January 1975.

13. Personal Communication with Mr. J. L. Hesse, Michigan Department of Natural Resources, Lansing, Michigan, April 1975.

14. Hesse, J. L., "Water Pollution Aspects of Polybrominated Biphenyl Production: Results of Initial Surveys in the Pine River in the Vicinity of St. Louis, Michigan," Presentation to the Governor's Great Lakes Regional Interdisciplinary Pesticide Council, 17 October 1974.

15. Personal Communication with Mr. James A. Cole, Chemical Samples Company, Columbus, Ohio, January 1975.

16. Personal Communication with Mr. Fred Fields, Bromine Products Manager, Ethyl Corporation, Baton Rouge, Louisiana.

17. Personal Communication with Mr. Phillip Lewis, Food and Drug Administration, Washington, D.C., January 1975.

18. Moore, D. E., J. F. Mills, and J. A. Schneider, "Bromination With Bromine Chloride Under Pressure," U.S. Patent 3,845,146, assigned to The Dow Chemical Company, Patented 29 October 1974.

19. Mitchell, L. C., "Process For Production of Polybrominated Aromatics," U.S. Patent 3,763,248, assigned to Ethyl Corporation, Patented 2 October 1973.

20. [illegible]kner, H., "Process For The Production of Bromine Derivatives of Aromatic Compounds," U.S. Patent 3,285,965, assigned to Chemische Fabrik Kalk G.m.b.H., Cologne-Kalk, Germany, Patented 15 November 1966.

21. Personal Communication with Dr. William C. Burnett, Regional Director of U.S. Department of Health, Education and Welfare, Food and Drug Administration Division, Kansas City, Missouri, February 1975.

22. Jackson, T. F., and F. L. Halbert, "A Toxic Syndrome Associated With the Feeding of Polybrominated Biphenyl-Contaminated Protein Concentrate to Dairy Cattle," J. Amer. Vet. Med. Assn., 165(5):437 (1974).

23. Isleib, D. R., and G. L. Whitehead, "Polybrominated Biphenyls: An Agricultural Incident and Its Consequences. I. The Agricultural Effects of Exposure."

Humphrey, H. E. B., N. S. Haynes, and M. L. Budd, "Polybrominated Biphenyls: An Agricultural Incident and Its Consequences. II. An Epidemiological Investigation of Human Exposure."

Technical Papers to be Presented at the 9th Annual Conference on Trace Substances in Environmental Health, University of Missouri, Columbia, 9-12 June 1975.

24. Willett, L. B., and H. A. Irving, "The Distribution and Clearance of Polybrominated Biphenyls by Cows," Technical Paper Scheduled for Presentation at 70th Annual Meeting of the American Dairy Science Association at Kansas State University, Manhattan, 22-25 June 1975.

25. Commerce Business Daily, Issue No. PSA-6276, p. 3. 11 March 1975.

26. Personal Communication with Mr. J. L. Hesse, Michigan Department of Natural Resources, Lansing, Michigan, 16 January 1975.

27. Hansen, D. J., P. R. Parrish, J. I. Lowe, A. J. Wilson, Jr., and P. D. Wilson, "Chronic Toxicity, Uptake, and Retention of a Polychlorinated Biphenyl (Aroclor 1254) in Two Estuarine Fishes," Bull. Environ. Contam. Toxicol., 6(2):113-119 (1971).

28. Nebeker, A. V., F. A. Publis, and D. L. Defoe, "Toxicity of Polychlorinated Biphenyls (PCB's) to Fish and Other Aquatic Life," EPA, National Water Quality Laboratory, Duluth, Minnesota (1971).

29. Personal Communication with Mr. James Dunphy, White Chemical Corporation, Bayonne, New Jersey, 23 December 1974.

30. Personal Communication with Mr. Patrick A. Lincoln, Waste Control Engineer, Michigan Chemical Corporation, St. Louis, Michigan, 16 May 1965.

31. Modern Plastics Encyclopedia, 51:10A, 1974-1975, October 1974.

32. Lyons, J. W., The Chemistry and Uses of Fire Retardants, Wiley-Interscience, a Division of John Wiley and Sons, Inc., New York, New York (1970).

33. Kerst, F., "Polybrominated Biphenyls," a Technical Presentation Concerning Operations of Michigan Chemical Corporation, St. Louis, Michigan, to the Michigan Environmental Review Board, 23 September 1974.

34. Personal Communication with Mr. Bill Raiman, Standard T Chemical Company, Staten Island, New York, 3 March 1975.

35. Personal Communication with Mr. Gerald Shaw, Standard T Chemical Company, Staten Island, New York, 24 March 1975.

36. Personal Communication with Mr. Robert Gilligan, Borg-Warner Corporation, Parkersburg, West Virginia, 30 March 1975.

37. Bhatnagar, V. M., Fire Retardant Formulations Handbook, Vol. I, Progress in Fire Retardancy Series, Technomic Publishing Company, Inc., Westport, Connecticut (1972).

38. Murray, R. W. "Combinations of Phosphonium Bromides and Brominated Aromatic Compounds as Flame Retardant Compositions for Olefin Polymers," U.S. Patent 3,699,077, assigned to American Cyanamid Company, Patented 17 October 1972.

39. Personal Communication with Dr. Chris Savides, American Cyanamid Company, Bound Brook, New Jersey, 21 April 1975.

40. Cyba, H. A., "Noval Flame Retardant Compositions of Matter," U.S. Patent 3,723,383, assigned to Universal Oil Products Company, Patented 27 March 1973.

41. Personal Communication with Mr. Ray Nelson, Universal Oil Products Company, Des Plaines, Illinois, 19 February 1975.

42. Green, J., and J. Versnel, "Self Extinguishing Composition," U.S. Patent 3,730,942, assigned to Cities Service Company, Patented 1 May 1973.

43. Personal Communication with Dr. Joseph Green, Cities Service Company, New York, New York, 19 February 1975.

44. Personal Communication with Mr. Phillip Schlamt, General Electric Company, Bridgeport, Connecticut, April 1975.

45. Jenkner, H., "Flameproofed Synthetic Resins," U.S. Patent 3,347,822 assigned to Chemische Fabrik Kalk G.m.b.H., Cologne-Kalk, Germany, Patented 17 October 1967.

46. Kolina, J. F., "There Are New Ways to Tame the Flame," Modern Plastics, pp. 42-45, May 1975.

47. Hill Top Research, Inc., Acute Toxicity and Irritation Studies Master BP-6 Hexabromobiphenyl (1970).

48. Norris, J. N., et al., "Toxicological and Environmental Factors Involved in the Selection of Decabromobiphenyl Oxide as a Fire Retardant Chemical," Ap. Poly. Symp. No. 22, pp. 195-219 (1973).

49. Aftosmis, J. G., et al., "The Toxicity of Brominated Biphenyls. I. Oral Toxicity and Embryotoxicity," Presented at the Society of Toxicology Meeting, March 1972.

50. Aftosmis, J. G., "Toxicology of Brominated Biphenyls. II. Skin, Eye, and Inhalation Toxicity and an Acute Test Method for Evaluating Hepatotoxicity and Accumulation in Body Fat," Presented at the Society of Toxicology Meeting, March 1972.

51. Cecil, H. C., J. Bitman, G. F. Fries, L. W. Smith, and R. J. Lillie, "PCB's in Laying Hens," Preprint Paper, National Meeting, Division of Water, Air, Waste Chemistry, Amer. Chem. Soc., 12(2):86-90.

52. Cecil, H. C., J. Bitman, R. J. Lillie, G. F. Fries, and J. Verrett, "Embryotoxic and Teratogenic Effects in Unhatched Fertile Eggs from Hens Fed Polychlorinated Biphenyls (PCB's)," Bull. Envir. Contam. Toxicol., 11(6):489-495 (1974).

53. Lillie, R. J., H. C. Cecil, J. Bitman, and G. F. Fries, "Differences in Response of Caged White Leghorn Layers to Various Polychlorinated Biphenyls (PCB's) in the Diet," Poultry Sci., 53:726-732 (1974).

54. Fries, G. F., L. W. Smith, H. C. Cecil, J. Bitman, and R. J. Lillie, "Retention and Excretion of Polybrominated Biphenyls by Hens and Cows," Presented at the 165th Meeting, American Chemical Society, Dallas, Texas, 11 April 1973.

55. Fries, G. F., and G. S. Morrow, "Excretion of Polybrominated Biphenyls into the Milk of Cows," Agricultural Environmental Quality Institute, U.S. Department of Agriculture, unpublished document.